D. Ultra-High-Resolution Electron Microscopy for Characterization of Catalyst Microstructures and Deactivation Mechanisms

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Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No.: DE-AC05-00OR22725

Objectives

- Develop and utilize new capabilities and techniques for ultra-high resolution transmission electron microscopy (UHR-TEM) to characterize the microstructures of catalytic materials of interest for reducing emissions of nitrogen oxides (NO_x) in diesel and automotive exhaust systems.
- Relate the effects of reaction conditions on the changes in morphology of heavy metal species on "real" catalyst support materials (typically oxides).

Approach

- Use new field emission microscope at the High Temperature Materials Laboratory to image catalyst particles at near-atomic level to characterize systematic series of model NO_x trap catalyst materials (composed of 2% platinum by weight on a mixed CeO_2-ZrO_2-La_2O_3-BaO-Al_2O_3 support material) and to develop techniques applicable for imaging future catalysts at sub-Ångstrom levels with the new Aberration-Corrected Electron Microscope (ACEM).
- Conduct studies of a series of NO_x trap catalyst specimens, provided by Ford Research Laboratory colleague Dr. G. Graham, that had been field-tested by running in vehicles with spark-ignition direct-injection (SIDI) engines, rather than by simulating exhaust compositions and cycles using bench-top reactors.

Accomplishments

- Characterized via high-resolution annular dark-field scanning TEM (STEM) imaging the structure of a model NO_x trap catalyst composed of 2% platinum by weight on a mixed CeO_2-ZrO_2-La_2O_3-BaO-Al_2O_3 support material. The imaging showed, for example, that initial dispersions of platinum species consisted of near-atomic clusters and "rafts" of platinum atoms one to 3 atomic layers thick.
- Characterized the progression of changes in the microstructure of NO_x trap catalysts as a result of vehicle aging, by TEM and STEM analysis of core samples taken from the centers of catalyst monoliths removed from the vehicles after 30,000, 53,000 and 82,000 km of driving.
- Successfully factory tested and subsequently accepted delivery of the ACEM, funded by the Office of Energy Efficiency and Renewable Energy. Achieved an Oak Ridge National Laboratory (ORNL) PEP milestone for

beneficial operation of all critical imaging systems and demonstrated the capabilities of the new microscope for imaging ultra-fine clusters of catalyst species on real catalyst samples of OFCVT interest.

Future Direction

- Use new high-resolution electron microscopy imaging techniques and energy-loss electron spectroscopy on the ACEM to characterize diesel particulate NO_x –reduction and lean NO_x trap samples in collaboration with Ford Research Laboratory colleagues.
- Develop new thrust capability for characterization of catalyst structures at the atomic level using the ACEM, using techniques of electron tomography. This will involve constructing a new specimen holder to allow high tilts (up to ±75 degrees), and assessing the ability of annular dark-field STEM imaging to provide unambiguous information on the shapes of fine catalyst particles and the shape changes that occur on aging.

Technical Progress

Microstructure of Pt/Mixed-Oxide Model Catalysts

A model NO_x trap catalyst composed of 2% platinum by weight on a mixed CeO_2-ZrO_2-La_2O_3-BaO-Al_2O_3 support material (or more formally, 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%$BaO.6Al_2O_3$)]) is being studied (in a separate task) to determine the effects of exposure to lean–rich exhaust mixtures on the microstructure of the catalyst. In the present task, the model catalyst material was characterized using the high-resolution annular dark-field imaging capability of the JEOL 2010F field emission TEM on loan as part of the new ACEM project. This effort served as a precursor to imaging of the ultrastructure of our catalyst samples using similar (but aberration-corrected) STEM imaging techniques on the ACEM.

The STEM/TEM instrument provides both bright-field TEM and dark-field STEM imaging capabilities, and typical results at the resolution level of the 2010F allowed the imaging of “rafts” of platinum species on the alumina/baria and ceria/zirconia phases of the experimental catalysts (e.g., Figure 1). However, the significantly higher resolution expected from the ACEM should permit unambiguous and more quantitative characterization of the exact structure of the as-dispersed precious metal species on both experimental and “real” catalyst samples. This will provide a better understanding of the initial stages of growth of catalyst particles under aging conditions, so that advances can be made in controlling heavy metal particle size changes with exposure to temperature and exhaust gas conditions.

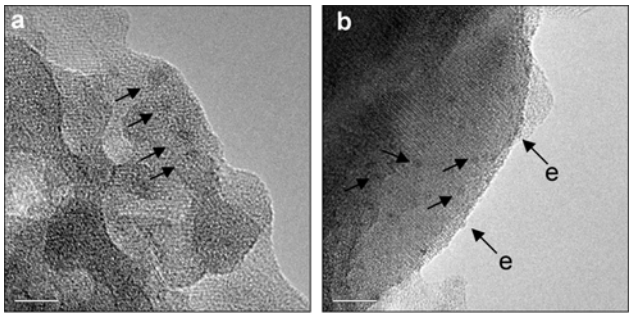

Figure 1. (a) Alumina phase with platinum rafts (arrows). (b) Ce-Zr phase with platinum rafts (arrows). Possible edge-on rafts are also shown (arrows labeled “e”). Scale = 5 nm

Microstructure of SIDI Vehicle-Tested Catalysts

In collaboration with Dr. George Graham of Ford Research Laboratory, we characterized a series of NO_x trap catalyst specimens that were field-tested by running in vehicles with SIDI engines. These catalysts comprised a double washcoat configuration on standard cordierite brick monoliths. The initial washcoat is composed of a baria-alumina composition on which platinum is dispersed at the 1 wt % level as the heavy-metal catalytic species. The second washcoat is composed of ceria-zirconia with rhodium dispersed at about the 0.2 wt % level. Catalyst core samples were taken from the centers of catalyst monoliths removed from the vehicles after 30,000, 53,000, and 82,000 km of driving, and their microstructures were compared with the microstructure of a fresh catalyst sample that had seen no vehicle aging.

The technique of “spectrum imaging” was used extensively to obtain quantitative information on the microstructural and chemistry changes on aging.

With this technique, an annular dark-field image is acquired from a chosen sample area. Then the same sample area is scanned point by point over a long time (up to hours, with drift correction implemented during the scan), with an energy-dispersive spectroscopy (EDS) spectrum acquired and saved at each point, to make the so-called spectrum image. In the present work, spectrum images of 512 × 384 pixel count (about 20 K spectra) were acquired, providing the ability to perform "principal component analysis" (PCA) with the data processing capabilities of the acquisition software. It is a way of identifying patterns in data and expressing the data in such a way as to highlight their similarities and differences. Patterns in data can be hard to find in data of high dimensions (i.e., a large number of points, each with an EDS spectrum), and PCA is a powerful tool for analyzing such data (details are beyond the scope of this report). A straightforward application is to extract "maps" of elements and phases from the spectrum image.

For example, an annular dark-field image from the 30,000-km catalyst sample is shown in Figure 2a. The EDS spectrum represented by the entire area of the image is shown in Figure 2c. The majority component is alumina, with cerium and zirconium also clearly present. The platinum component is essentially in the noise at this full scale, but the platinum L family is clearly present, as indicated in Figure 2d, with no overlaps of other elements. When a window is applied to show only the counts from the platinum L family, as shown in Figure 2b, the one-to-one correspondence between the bright-contrast particles in the annular dark-field image and the high-density platinum concentrations in the platinum image (as marked by arrows) clearly confirm the location and size distribution of platinum in the specimen area.

A similar result from the 82,000 km sample is shown in Figure 3a, which shows platinum particle growth as a result of aging phenomena during the extended driving cycle. A benefit of the spectrum imaging process is that the presence of any minor components in an image area can be determined. In the case of these SIDI catalysts, rhodium is supposed to be present at about 10% of the level of the platinum (i.e., at the 0.1 wt % level), but in the images acquired to date, no rhodium was identified (all the bright contrast particles in any image acquired corresponded to platinum). It is likely that either

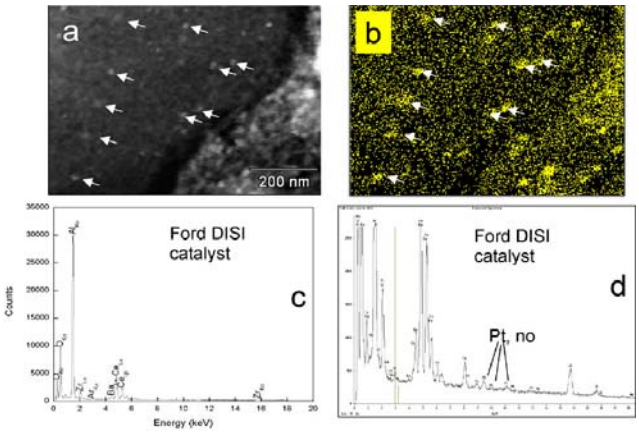

Figure 2. (a) Annular dark-field image of 30,000-km SIDI catalyst. (b) Platinum map extracted from sum spectrum of Fig. 2c. (c) Sum spectrum from spectrum image collection. (d) Expanded sum spectrum showing clear platinum peaks.

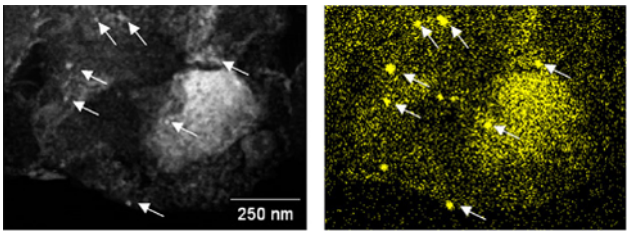

Figure 3. (a) Annular dark-field image of catalyst area in 82,000-km SIDI sample. (b) Platinum map extracted from spectrum image. Note the ability to locate the platinum particles unambiguously, even in the presence of a large bright-contrast aggregate of Ce-Zr in the center of the image (the increased contrast in this area in the platinum map is due to an increase in the background from the high-atomic-number material).

rhodium is atomically dispersed even after significant aging in the test vehicles, or it is present in widely isolated particles that will require further analysis to locate. Data such as these are providing a significant input to the understanding of the effects of vehicle aging of NO_x trap catalysts.

Ultra-High Resolution Imaging of Catalyst Clusters Using the ACEM

ORNL's ACEM (Figure 4) was delivered in May 2004 and installed in the newly constructed Advanced Materials Characterization Laboratory. The instrument is one of the first two combination STEM/TEM instruments in the country that are

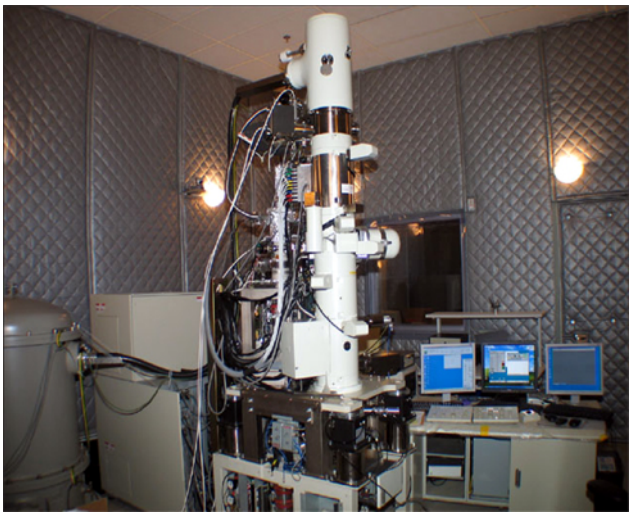

Figure 4. ORNL's ACEM, the JEOL 2200FS-AC, during final assembly and test-out. The instrument will ultimately be operated from the adjacent control room (seen through window behind the instrument).

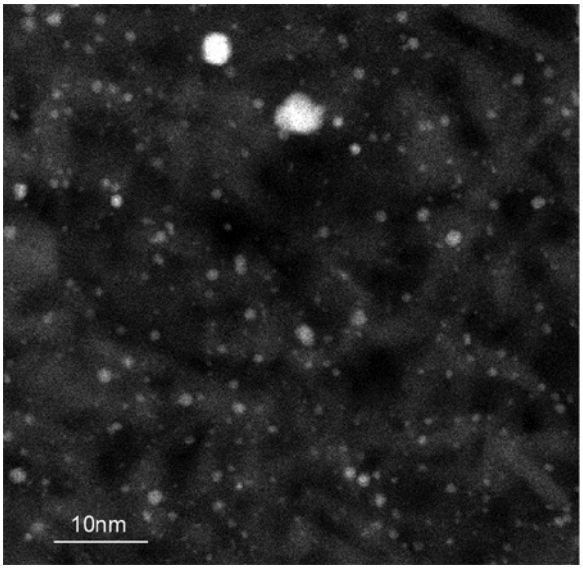

Figure 5. Example of an early very high-resolution annular dark-field image of platinum species on alumina support. The finest bright spots represent platinum clusters of a few atoms, with perhaps single atoms also seen.

equipped with a special corrector element on the illumination to enable a probe size of 0.7Å (compared with a 1.4-Å probe in the uncorrected instrument). This increase in probe resolution results in a 10-fold improvement in contrast in STEM dark-field imaging mode and should enable resolution of heavy metal species such as platinum on light oxide support materials at the single-atom level. An early result from the ACEM is the annular dark-field image shown in Figure 5, which is from a sample of as-deposited platinum on alumina. The platinum particles show in bright contrast; the two large particles are in the 2.5–4 nm size range (and are the only two particles visible unambiguously in standard bright-field images). The finest spots may be single atoms of platinum, or at most clusters of two or three atoms. The image illustrates the advanced capability the ACEM will provide for future catalyst characterization.

Analysis of catalyst materials at ultra-high resolution provides the potential to characterize directly the shapes of nanometer-sized particles and their changes with aging. The ultimate goal is to obtain a full understanding of the mechanisms of catalyst activity, selectivity, and aging. In parallel work to the development of advanced imaging techniques in the laboratory, we are collaborating with Lawrence Berkeley National Laboratory in a computational component of the work that involves modeling catalyst particles and calculating the images expected from them (conventional TEM images have been simulated so far, with STEM images to be done in the future). It is of great interest to determine, with very small particles comprising only a relatively few atoms, what crystal facets are exposed at the surface from the initial fine particle dispersions to larger particles as the catalyst ages. A typical model is shown in Figure 6, along with the corresponding computed TEM image and a chosen line profile that illustrates that, in the ideal case, there is a one-to-one correspondence between image intensity and the number of atoms in a column. This suggests that real atomic structure images of a particle taken from different directions (i.e., in a tomography application) might allow unambiguous characterization of the exact particle shape, with the specific crystal planes exposed on the surface thereby analyzed. A new research thrust area is being developed to implement the capability and techniques for nanoparticle shape determination with sub-Ångstrom imaging in the ACEM.

Conclusions

The acquisition and imminent beneficial operation of the ACEM will provide OFCVT programs with the top capability in the nation for characterization of catalyst materials and other materials of in-

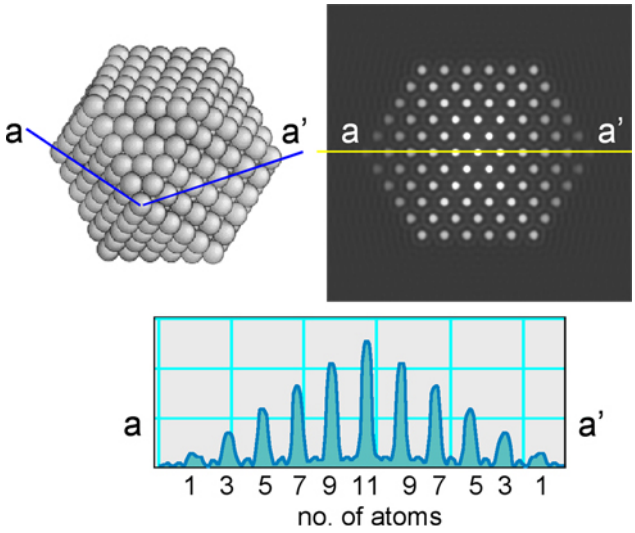

Figure 6. Example of model catalyst particle imaging computation. A cuboctohedron particle geometry is shown, with the image of the particle looking down the plane of a-a'. A line trace thru the image shows a direct relationship between atom column intensity and the number of atoms in each column.

terest to the program. Imaging at the single-atom level of heavy catalyst species on oxide substrates—coupled with electron spectroscopy to obtain, for example, chemical binding information—will add a new dimension to our understanding of the behavior of these complex materials. The present work using ORNL's current TEM and STEM instruments, with techniques such as annular dark-field imaging and especially spectrum imaging, has paved the way for rapid implementation of the next level of imaging and analysis capabilities. Both model NO_x trap catalysts and catalysts run in vehicles for known times have been characterized. Changes in platinum particle sizes and the relationship between the various oxide support species upon aging have supplied information on the mechanisms of catalyst degradation. Finally, initial work on modeling of catalyst particle shapes and the resulting images has shown promise for allowing the determination of particle morphologies (exposed crystal facets) with high-resolution electron tomography using the ACEM.

Publications/Presentations

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